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APPLICATIONS OF DIDECMP EXTRACTION CHROMATOGRAPHY TO NUCLEAR ANALYTICAL CHEMISTRY

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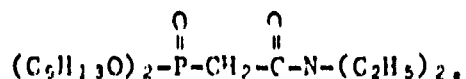
ABSTRACT

Dihexyl-N,N-diethylcarbamylmethylenephosphonate (DHDECMP) is a highly selective extractant for actinides and lanthanides. This reagent, extensively studied for process-scale operations, also has valuable analytical applications. Extraction chromatographic columns of DHDECMP, supported on inert, porous, polymer beads effectively separate most metallic impurity elements from the retained inner transition elements. The retained elements can be separated into individual fractions of (1) lanthanides, (2) americium, (3) plutonium, and (4) uranium by mixed-solvent anion exchange.

INTRODUCTION

Highly pure actinides are required in nuclear reactor fuels and radioisotope power generators, and as targets or sources in experimental measurements of nuclear constants. Prior separation of the actinide matrix from the impurities improves the accuracy of most analytical methods for trace elements. It is essential to attain the sensitivity limits of multielement techniques such as emission spectrography and inductively-coupled-plasma (ICP) emission spectrometry.

Dihexyl-N,N-diethylcarbamylmethylenephosphonate (DHDECMP),
the organophosphate bidentate



is a highly selective extractant for actinides and lanthanides.¹⁻³ Its potential as an analytical reagent, however, has been neglected by most prior investigators. In recent

literature, only Baker⁴ has reported application of DHDECMP to analytical-scale separations.

At Los Alamos we routinely use extraction chromatographic columns of DHDECMP, supported on Chromosorb-102 beads, to separate most metallic impurity elements from actinide matrices before the impurities are measured by emission spectrography. Navratil⁵ reports that 33 elements can be extracted into DHDECMP from 7M HNO₃ with extraction coefficients of less than unity and therefore can be separated readily from an actinide matrix. The separation is applicable to uranium, plutonium, trivalent actinides, or mixed actinide materials.

SOURCES AND PURIFICATION OF REAGENTS

DHDECMP

Because extraction with DHDECMP is influenced by reagent purity, the variation in distribution coefficients reported in the literature is not surprising; it probably is attributable to purity differences in the DHDECMP used by the experimenters.

Wateree Chemical Company, Lugoff, SC, supplies DHDECMP of a nominal 50% purity. Bray Oil Company, Los Angeles, which offers DHDECMP of ~85% purity, is investigating a process that will upgrade the purity to >95%. The DHDECMP used in our investigation was produced to ~95% purity, on a special order, by Organometallics, Inc., East Hampstead, NH.

DHDECMP may be purified of the corresponding dihexyl ester of phosphoric acid by acid hydrolysis, followed by passage through a column of Amberlite A-26 (hydroxide-form).⁶ A more comprehensive purification, developed by Schroeder,⁷ reacts DHDECMP with mercuric nitrate to form a precipitate of Hg(DHDECMP)NO₃. Mercury is dissociated from this salt by preferential complexation with basic cyanide, whereupon the liberated DHDECMP is extracted into hexane and repeatedly washed free of mercuric cyanide with water. Finally, the hexane is distilled away under reduced pressure to yield the purified DHDECMP.

Chromosorb-102 Beads

Extraction chromatography combines the benefits of liquid-liquid solvent extraction with the advantage of multi-stage operation, in which components having relatively small differences in distribution coefficients can be separated easily and completely. Extraction chromatography has been

studied at Rockwell International, Rocky Flats Plant, as a plant process for recovering americium.⁶ Of more than 30 support materials evaluated, the Rocky Flats study recommends Amberlite XAD-4, a macroporous nonionic, polystyrene-divinylbenzene copolymer. Unfortunately, the only commercially available XAD-4 beads are 20 to 50 mesh, a size much too coarse for use in analytical-scale columns. Our attempt to convert the XAD-4 beads to an appropriate size by grinding and sieving contributed unacceptably high levels of metallic impurities.

However, Chromosorb-102, a macroporous polymer material similar to Amberlite XAD-4, is available in several mesh sizes. Johns-Manville, Denver, supplied the 120 to 200 mesh fraction used in our investigation.

Chromosorb-102, as received, is insufficiently pure for use in separating trace metallic impurities for analysis. The impurities in Chromosorb-102 beads are reduced to acceptable levels by the following procedure. First, the beads are soaked overnight in an equal-volume mixture of 6M HCl and methanol and are separated from the solution by vacuum filtration. (Methanol is necessary to wet the hydrophobic beads.) The soak/filtration cycle is done twice again. The purified beads are washed with an equal-volume mixture of methanol and high-purity water until no HCl odor is discernable. Finally, the beads are washed with anhydrous methanol to remove residual water and are separated from the solution by vacuum filtration. After being dried to constant weight in a vacuum desiccator, the beads are ready to be coated.

PREPARATION OF BEADS AND COLUMNS

DHDECMP-Coated Beads

The purified, dried Chromosorb-102 beads are coated with DHDECMP by the following procedure. First, 33 g of ~95% pure DHDECMP is weighed into a clean 400-ml beaker, diluted to ~120 ml with pure hexane, and mixed thoroughly. Then 50 g of beads are added slowly and in small increments. Sufficient time must be allowed for each increment of beads to become saturated with liquid before adding more. Next, the hexane is evaporated from the immersed beads, first in air and then under vacuum, to a final weight of 83 g. The DHDECMP-coated beads should have the appearance and pouring characteristics of a dry powder.

Chromatographic Columns

The chromatographic columns are prepared by the following procedure. The hemispherical top of a 3-ml polyethylene

dropper (Cole-Parmer No. C-6226-02 or equivalent) is removed so that the dropper becomes a 6-x 100-mm column with a reservoir. A small portion of quartz wool is inserted in the tip of the column to support the coated beads. Next, 1.5 g of the DHDECMP-coated beads are transferred to the column and the side of the column is tapped until the bead level settles to ~6 mm below the reservoir. Another portion of quartz wool is inserted in the column above the bead bed.

Air is displaced from the bead bed by gently backfilling the column with water from a disposable, plastic hypodermic syringe connected to the column by flexible 1/8-in. i.d. tubing. When the entire bead bed and upper quartz wool plug have been wet (without dislodging the beads), the syringe is disconnected.

The filled column is pretreated by washing it sequentially with 6 ml of distilled water, 6 ml of 0.1M HNO_3 , and 6 ml of 5.5M HNO_3 . The column now is ready for use.

EXPERIMENTAL

The extractability of various ions by DHDECMP is highly dependent on the aqueous acid medium from which they are extracted. Uranium is extracted preferentially from hydrochloric acid over a wide concentration range (Fig. 1); however, the relatively high solubility of DHDECMP in this acid precludes its use as the extractant in chromatographic columns. In extractions from perchloric acid (Fig. 2), the distribution coefficients of all actinides and lanthanides exceed 500 over the range of 0.1-8M HClO_4 ; however, many other elements also are highly extracted.

In most reported investigations using DHDECMP, extractions have been from nitric acid. The solubility of DHDECMP in this acid is only 0.4 g/liter,⁸ a value sufficiently low to be compatible with extraction chromatography.

Our extraction data from

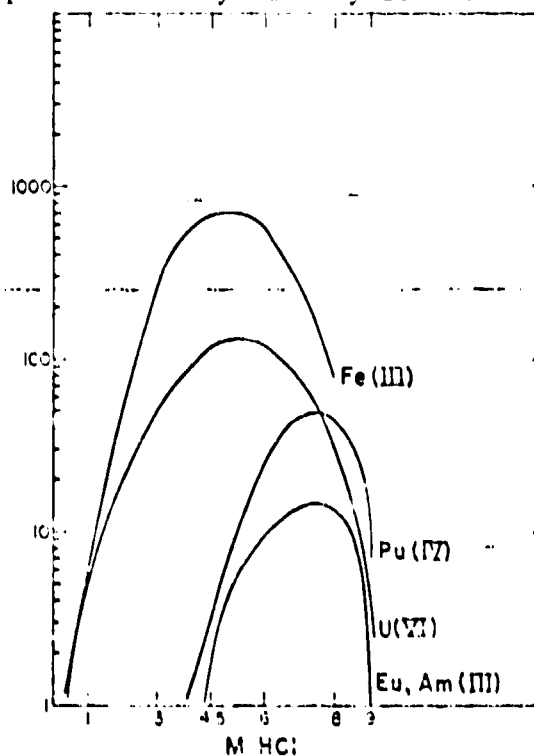


Figure 1. Extraction from HCl into DHDECMP

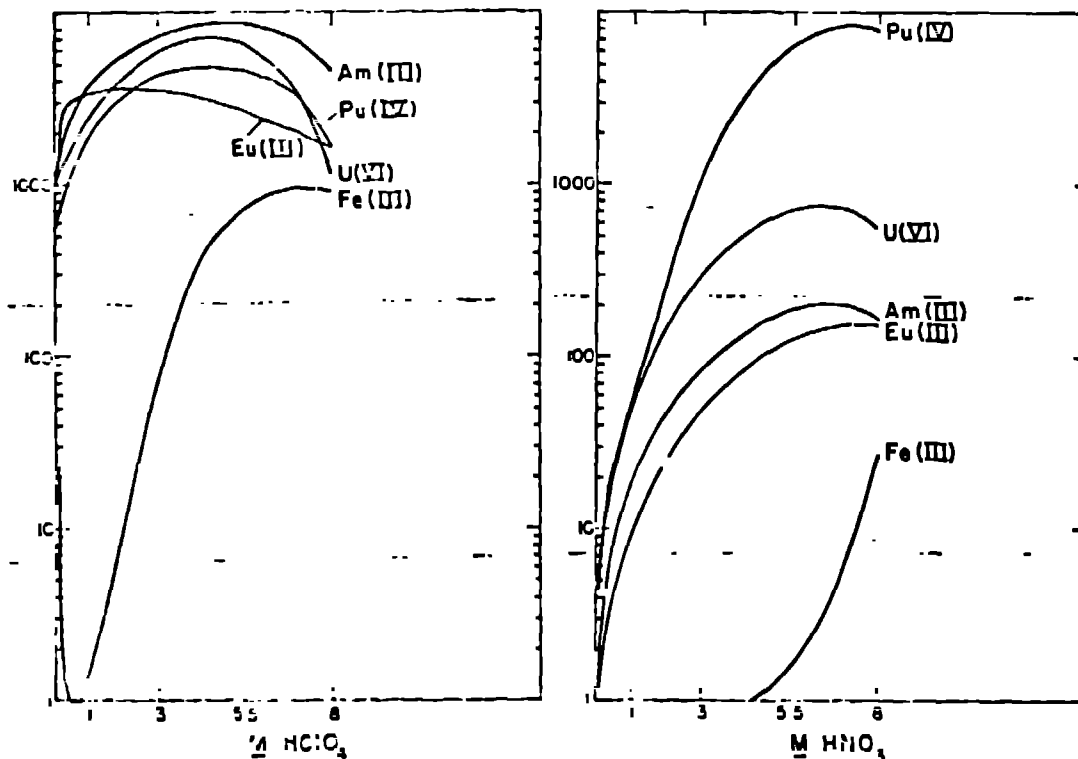


Figure 2. Extraction from HClO₄ into DHDECMP

Figure 3. Extraction from HNO₃ into DHDECMP

nitric acid (Fig. 3) show Pu(IV) > U(VI) > Am(III) ≈ Eu(III), with all distribution coefficients being >100 over the range of 4-8M HNO₃. Iron is extracted only weakly below 6M HNO₃. Because nitric acid offers high selectivity for actinides and lanthanides, and low solubility of DHDECMP, we selected it for the initial separation of most other elements.

Figure 4 shows the elements retained and those eluted in 5.5M HNO₃ from DHDECMP chromatographic columns, prepared as described previously. A few elements were only partially extracted; these elements might be either completely extracted or completely retained in a somewhat different concentration of nitric acid. The retained elements then are eluted with hydrochloric acid plus hydrofluoric acid for recovery (Figure 5) or additional chemical separations (Figure 6).

PROCEDURES FOR CHEMICAL SEPARATION

A. Separation of Impurities from Actinides (and Lanthanides)

1. Prepare an extraction chromatographic column of DHDECMP-coated beads as described earlier.
2. Place an appropriate receiver under the column, and transfer to the column ~1 ml of 5.5M HNO₃ containing not more

suitable container for recovery or additional separation with 12 ml of 0.3M HCl-0.01M HF.

B. Separation of Individual Actinides from the Lanthanide Group

The separation of individual actinides is based on anion exchange. The procedure uses the hydrochloric acid-acetone medium reported by Orlandini⁹ to separate lanthanides from trivalent actinides and the aqueous hydrochloric acid system used at Los Alamos for routine separations of americium, plutonium, and uranium.¹⁰

1. Add 5 drops of 6M HClO₄ to the column eluate (from Step A.5) and evaporate the solution to dryness.
2. Prepare a fresh 25 vol% 12M HCl-acetone mixture.
3. Prepare a fresh 60 vol% 12M HCl-acetone mixture. Keep both mixtures capped to minimize acetone evaporation.
4. Prepare a 6- x 60-mm ion exchange column from a 1.6-ml polyethylene dropper (Cole-Parmer No. C-6096-00 or equivalent) by removing the uppermost layer of plastic to form an open reservoir and column. Insert a small portion of quartz wool in the tip to support the resin.
5. Add to the column a slurry consisting of Bio-Rad AGMP-1, macroporous, 50 to 100 mesh, anion exchange resin (or equivalent) in the 25% HCl-acetone solution. Continue adding slurry until the settled resin height is just below the reservoir.
6. Pretreat the anion exchange resin by passing 5 ml of 25% HCl-acetone through the column. (Cover the column with an inverted beaker to minimize evaporation.)
7. Place an appropriate receiver for the lanthanide fraction under the column.
8. Dissolve the dried residue (from Step B.1) with a 1-ml portion of 25% HCl-acetone and transfer to the column. Allow this solution to drain completely, then rinse the residue container twice with 1-ml portions of 25% HCl-acetone and transfer each portion to the column.
9. Complete the elution of the lanthanide fraction by passing another 15 ml of 25% HCl-acetone through the column.
10. Place an appropriate receiver for the americium fraction

under the column.

11. Elute the americium with 4 ml of 60% HCl-acetone, followed by 8 ml of aqueous 12M HCl. (The 60% HCl-acetone provides an intermediate step in the transition from 25% HCl-acetone to aqueous 12M HCl; without it gas bubbles form and plug the resin column.)
12. Place an appropriate receiver for the plutonium fraction under the column.
13. Elute the plutonium with 4 ml of 12M HCl-0.1M HI. Allow 10 minutes for complete reduction of plutonium to Pu(III) by iodide. Then elute the remaining plutonium with another 6 ml of 12M HCl-0.1M HI.
14. Place an appropriate receiver for the uranium fraction under the column.
15. Elute the uranium from the column with 8 ml of 0.1M HCl.

ADDENDUM

As this paper was being written, we received a sample of Lewatit E803/81, a proprietary extractant resin containing Los Alamos-supplied DHDECMP. The resin, provided by Mobay Chemical Corporation, Pittsburgh, Pa., was prepared for our evaluation by Bayer AG, a German affiliate. The extractant resin beads range in size from 25 to 140 mesh, with most in the 60 to 70 mesh range. Because the extractant is incorporated into the beads as they are polymerized, the DHDECMP load is quite high, 310 g/liter of resin. Based on our preliminary evaluation, a 6- x 100-mm column of either Chromosorb or Lewatit resin retains >99.99% of 15 mg of americium. The Lewatit resin has the higher capacity, because its DHDECMP load is about 1.5 times that of the Chromosorb. However, its larger bead size makes the Lewatit resin somewhat less suitable for analytical-scale columns.

ACKNOWLEDGMENT

Alexander J. Siber of Mobay Chemical Corporation provided the sample of Lewatit E803/81 extractant resin.

REFERENCES

1. W. W. Schulz and L. D. McIsaac, "Bidentate Organophosphorus Extractants: Purification, Properties, and Applications to Removal of Actinides from Acidic Waste Solutions," Proc. Int. Solvent Extraction Conf., Toronto, Canada,

September 9-16, 1977.

2. J. D. Navratil and G. H. Thompson, Nucl. Techn. 43 136-145 (1979).
3. L. D. McIsaac, J. D. Baker, J. F. Krupa, R. E. LaPointe, D. H. Meikrantz, and N. C. Schroeder, "Study of Bidentate Compounds for Separation of Actinides from Commercial LWR Reprocessing Wastes," Idaho National Engineering Laboratory report ICP-1180 (February 1979).
4. J. D. Baker, R. J. Gehrke, R. C. Greenwood, and D. H. Meikrantz, Radiochim. Acta 28 51-54 (1981).
5. J. D. Navratil, "Chemical Research at Rocky Flats," Rockwell International Corporation report RFP-2774 (February 1978).
6. C. E. Alford and J. D. Navratil, "Evaluation of Extraction Chromatography for Americium Recovery," Rockwell International Corporation report RFP-2625 (March 1977).
7. N. C. Schroeder, L. D. McIsaac, and J. F. Krupa, "Purification of Dihexyl-N,N-diethylcarbamylnmethylenephosphonate by Mercury (II) Precipitation," Exxon Nuclear Idaho Company report ENICO-1026 (January 1980).
8. L. D. McIsaac, J. D. Baker, J. W. Tkachyk, "Actinide Removal from ICPP Wastes," Idaho National Engineering Laboratory report ICP-1080 (1975).
9. K. A. Orlandini and J. Korkisch, "Anion-Exchange Behavior of Transplutonium Elements and Lanthanides in Hydrochloric Acid-Organic Solvent Mixtures," Argonne National Laboratory report ANL-7415 (January 1968).
10. S. F. Marsh, M. R. Ortiz, R. M. Abernathey, and J. E. Rein, "Improved Two-Column Ion Exchange Separation of Plutonium, Uranium, and Neodymium in Mixed Uranium-Plutonium Fuels for Burnup Measurement," Los Alamos Scientific Laboratory report LA-5568 (June 1974).